Competing intermolecular and intramolecular hydride transfers in the ionic hydrogenation of (2-alkoxyphenyl)di(1-adamantyl)-methanols †

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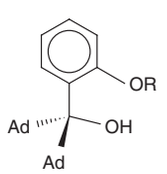
Received (in Cambridge) 26th April 1999, Accepted 15th June 1999

ortho-Lithiation of anisole followed by reaction with di(1-adamantyl) ketone gives *syn*-(2-anisyl)di(1-adamantyl)-methanol with the C–OH proton intramolecularly hydrogen-bonded to the methoxy group. Reaction of the alcohol with trifluoroacetic acid (TFA) in dichloromethane leads to a trifluoroacetate and a substituted phenol. These are formed *via* a carboxonium ion, resulting from an intramolecular 1,5-hydride shift of the initially formed carbocation. Ionic hydrogenation of the alcohol with TFA and a hydrosilane in dichloromethane results in the expected *anti* and *syn* deoxygenation products as well as the trifluoroacetate and the phenol. *anti*-(2-Anisyl)diadamantylmethane (benzylic hydrogen remote from methoxy, confirmed by a single crystal X-ray diffraction study) is formed directly from the carbocation while the *syn* isomer results from reduction of the carboxonium ion. Reduction of the carbonium ion is more hydrosilane-selective than that of the carboxonium ion. Kinetic isotope effects (k_H/k_D) on the reaction of the carbocation at room temperature average 1.50 for triethylsilane and dimethylphenylsilane. Analogous reaction of the (2-ethoxyphenyl) derivative gives only *syn*-(2-ethoxyphenyl)diadamantylmethane and the substituted phenol. Kinetic isotope effects on the reduction of the corresponding carboxonium ion average 1.34 for the same hydrosilanes.

Introduction

The chemistry of compounds containing 1-adamantyl groups[1] is often characterized by the rigidity and integrity of these groups. Because of their rigidity, adamantyl groups are sterically more demanding than *tert*-butyl, for example, and tend to increase rotation barriers in molecules where conformational isomerism occurs, making it possible to isolate rotamers as distinct species, stable under normal experimental conditions.[2–5] Furthermore, they have a marked tendency to conserve their structural identity regardless of what is happening at the carbon atom to which they are attached. For this reason the tri(1-adamantyl)methyl radical[6] and cation[7] are persistent, and *o*-tolyldi(1-adamantyl)methyl cations are relatively stable species which can be studied at room temperature.[8,9] Other aryldi(1-adamantyl)methyl cations can be observed at low temperaures in superacid media.[10] Aryl- or heteroaryldi-(1-adamantyl)methyl derivatives owe much of their unusual chemistry to the fact that the adamantyl groups tend to be located on either side of the ring plane, though not usually symmetrically, and that a fourth substituent to the methyl carbon or, in the case of carbocations, the vacant orbital, is necessarily close to the ring plane. This favours intramolecular hydrogen bonding in (2-pyridyl)diadamantylmethanols[11] and hydride transfer from a suitable *ortho*-alkyl substituent to the aryldiadamantylmethyl cation.[12]

Aromatic ethers such as anisole are lithiated at the *ortho* position by exchange with *n*-butyllithium.[13] It occurred to us that this might be an interesting starting point for the further investigation of hydrogen bonding and possible hydride transfer in alcohols bearing an alkoxy group. In this paper the synthesis and reactions of (2-anisyl)di(1-adamantyl)methanol, **1S-Me**, and, more briefly, of its (2-ethoxyphenyl) analogue,



1S-Me
1S-Et

1S-Et, are described. First we shall consider their structures and then the reactivity of the corresponding carbocations. When carbocations are generated from alcohols in the presence of various hydride donors, such as hydrosilanes, they are reduced in a reaction generally known as "ionic hydrogenation" to give products of alcohol deoxygenation.[14] This has proved to be an interesting means of investigating the stereochemistry of intermolecular hydride transfer in conformationally locked systems.[15]

Results and discussion

Alcohol synthesis and structure

ortho-Lithiation of anisole[16] by means of *n*-BuLi–TMEDA in diethyl ether or THF, followed by reaction with di(1-adamantyl) ketone, gives the corresponding (2-anisyl)diadamantylmethanol, **1S-Me**, as a single isomer in good yield. ^{1}H NMR (δ_H of OH = 6.58 ppm in chloroform) and IR spectra (ν_{OH} 3499 cm^{-1}) of the product show clearly that the alcohol proton is intramolecularly hydrogen-bonded and, therefore, that it is the *syn* rotamer with the OH group in proximity to the alkoxy substituent. The position of the ^{1}H NMR signal varies by less than

† Details of all KINAL calculations (Tables 5S and 6S) are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/1999/1639, otherwise available from BLDSC (SUPPL. NO. 57589, pp. 2) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

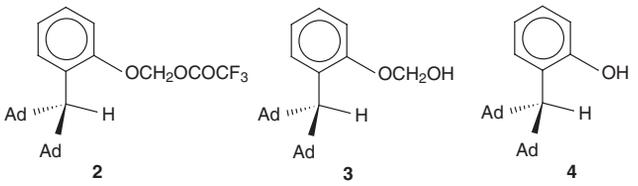
0.002 ppm when the concentration is reduced 1000-fold from 0.13 M, is almost independent of the solvent, and has a low temperature coefficient (−1.6 ppb °C^{-1}) as in the 2-pyridyl analogues.[11] The (2-ethoxyphenyl) derivative, **1S-Et**, prepared in the same way as **1S-Me**, shows very similar NMR and IR characteristics, with the NMR shift of the alcohol proton slightly greater (6.79 ppm in chloroform) and the IR ν_{OH} slightly lower (3480 cm^{-1}). The differences between the IR maxima of **1S-Me** and **1S-Et** and those of free OH groups are much more modest than the corresponding differences in the ^{1}H NMR signals of the OH protons, which means that these alcohols would not fit the previously established NMR–IR correlation, essentially based on OH · · · N hydrogen bonds in pyridyl and thiazoyl derivatives.[11]

These results are consistent with previous work which shows that relatively strong hydrogen bonding occurs in α,α-disubstituted *o*-methoxybenzyl alcohols.[17] In the di(*tert*-butyl) derivative the hydrogen bond formation enthalpy, estimated by studying the temperature dependence of the bonded and free IR absorptions at 3508 and 3616 cm^{-1}, amounts to 1.4 kcal mol^{-1}.‡ The ν_{OH} of **1S-Me** and **1S-Et** at 3499 and 3480 cm^{-1}, respectively, implies slightly stronger hydrogen bonds; we were unable to locate the absorption of free OH.

Molecular mechanics [MM2(85)] calculations[18] on the steric energies of the 2-anisyl alcohol, **1-Me**, make the *syn* isomer 1.8 kcal mol^{-1} more stable than the *anti*. This is a much smaller difference than for the corresponding 2-methyl (7.0 kcal mol^{-1})[3b] or 2-ethyl (70.9[12] − 63.7 = 7.2 kcal mol^{-1}) derivatives, which suggests that the effective size of the methoxy group is less than that of either. The molecular mechanics calculation does not take into account hydrogen bonding, which means that the real energy difference between the rotamers must be, according to previous work,[17] greater by probably slightly more than 1.4 kcal mol^{-1}. An attempt to determine the structure of the alcohol by X-ray diffraction was not totally successful.[19] There is one disordered dichloromethane molecule for two **1S-Me** molecules (confirmed by elemental analysis) and the structure failed to converge to an acceptable *R* value. All other atoms were located either directly or from the Fourier difference map. The H · · · O and O · · · O distances are 1.47 and 2.55 Å, respectively, and the O–H · · · O angle is about 168°. These are fairly typical values for this type of hydrogen bond.[20] All other features are typical of aryl- and heteroaryldiadamantylmethyl derivatives previously studied.[4,5,12]

Trifluoroacetylation of *syn*-(2-anisyl)di(1-adamantyl)methanol, 1S-Me

The alcohol was treated with TFA (4% v/v) in deuteriated dichloromethane in an NMR tube at 25 °C. The addition of TFA causes no colouration but the immediate disappearance of the proton signal at 6.58 ppm and a small downfield displacement of the aromatic and methyl group proton signals. The first-order rate constant, k_{exp}, based on the progressive disappearance of the methyl signal is about 7×10^{-4} s^{-1}, this value being little affected by trifluoroacetic anhydride (TFAA), added to the medium in order to scavenge adventitious water or that produced by reaction of the alcohol. The methyl signal is replaced by CH_2 and benzylic CH signals at 6.00 ppm and 2.84 ppm, respectively. The two groups were further identified by ^{13}C NMR (corresponding signals at 89.9 and 56.5 ppm, respectively). The values for the proton and carbon shifts of the CH_2 group are closely similar to those reported for aryloxymethyl benzoates[21] and alkoxymethyl acetates,[22] respectively, and clearly indicate that the methoxy group is trifluoroacetylated at the same time as the alcohol is deoxygenated, to give a trifluoroacetate, **2**. Inspection of the proton spectrum taken after about 10 half-lives reveals complete conversion to trifluoroacetate (about 90%) and a minor product, associated with ^{13}C NMR signals indicating the presence of a CH_2 group, a benzylic CH, three (of presumably 4) aromatic CH groups and two quaternary aromatic carbons. These data are compatible with a substituted phenoxymethanol, **3**, but, unfortunately, no comparable data are available in the literature and, moreover, the product could not be isolated.



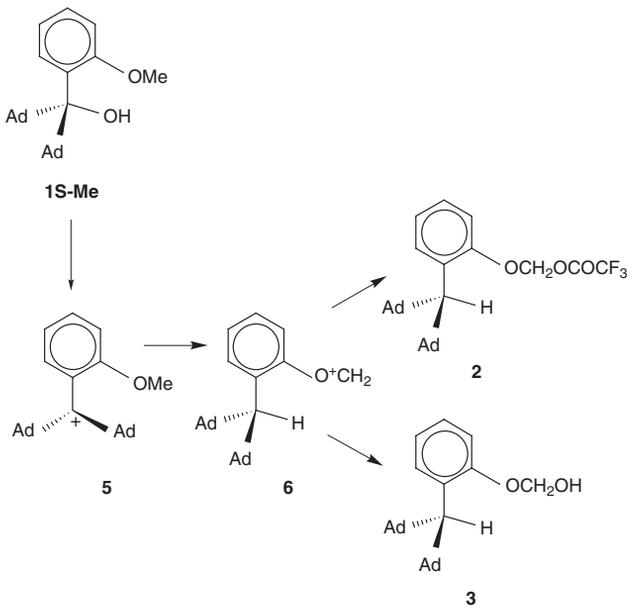
Treatment of the alcohol with TFA in dichloromethane followed by conventional aqueous work-up gives the trifluoroacetate, **2**, and a phenol, **4**, in the same proportions as **2** and **3** in the NMR experiment. The two products are separable by gas chromatography on a capillary column and give appropriate ion trap detector (ITD) spectra, the molecular ion being, however, very weak even with chemical ionization. The trifluoroacetate is converted to the same phenol upon chromatography, being hydrolysed by the acidic silica gel. In chloroform the ^{13}C NMR shifts of the benzylic carbons in **2** and **4** are 56.1 and 57.2 ppm, respectively. These values are to be compared with values of about 60 ppm for a benzylic group with the hydrogen oriented towards various modified *ortho* ethyl and isopropyl groups, whereas the opposite orientation is associated with a shift of 74 ppm.[12]

Molecular mechanics calculations on the steric energies of the rotamers which would be produced by simple deoxygenation of the alcohol **1S-Me** make the *syn* more stable than the *anti* isomer by 2.1 kcal mol^{-1}, while the *syn* phenol is estimated to be 2.4 kcal mol^{-1} more stable than the *anti* rotamer, and similar differences can be assumed for the phenoxymethanol and trifluoroacetate rotamers. The NMR spectra and calculation establish therefore that compounds **2**, **3** and **4** are the *syn* rotamers. Identification of these materials as the *anti* isomers would conflict with the NMR data and also require a totally implausible rotation to a less stable isomer.

A reasonable interpretation of these results is that formation of the (2-anisyl)diadamantylmethyl cation, **5**, is followed by 1,5-hydride transfer from the adjacent methoxy group to the *syn* face of the cation with the formation of an oxygen-stabilized carboxonium ion, **6**.[23] This latter is then attacked by trifluoroacetate ion to give trifluoroacetate, **2**, or by water, either adventitious or formed at the same time as the carbocation, to give the phenoxymethanol, **3** (Scheme 1). Analogous results have been reported for phenyldiadamantylmethanols with 2-ethyl or 2-isopropyl substituents, where carbocation formation is followed by 1,4-hydride transfer, to give various products with a modified *ortho* substituent.[12] 1,5-Hydride shifts are more common than 1,4-, probably because it is easier to attain the appropriately short C$^+$ · · · H distance in the larger system and to satisfy the stereoelectronic requirements of the transition state.[24] In the present case, the overall reaction is qualitatively slower than that of the ethyl or isopropyl derivatives,[12] but this is related to the rate at which the respective carbocations are formed and has no bearing on the relative rates of 1,4- and 1,5-hydride shifts.

Aryloxymethyl cations do not appear to have been described previously but alkoxymethyl cations have long been proposed as intermediates in the solvolysis of acetals, alkoxymethyl esters and chloromethyl ethers,[25,26] and have been directly observed by NMR at low temperature.[23b] They are also formed by 1,6- and higher order hydride shifts in the gas-phase, but not the solution-phase, reactions of $CH_3O(CH_2)_nSCH_2^+$.[26] A 1,5-hydride shift from an ethoxy group to a carbocation has also been reported.[27]

‡ 1 cal = 4.184 J.



Scheme 1

Reaction of **1S-Et** under the same conditions as for **1S-Me** gives the phenol, **4**, and acetaldehyde directly. At no time is there an NMR signal corresponding to a trifluoroacetate.

Competing trifluoroacetylation and ionic hydrogenation

***syn*-(2-Anisyl)di(1-adamantyl)methanol.** *(i) General aspects.* A much-used method for alcohol deoxygenation, known as ionic hydrogenation, involves hydrosilane reduction of the carbocation generated in TFA–dichloromethane.[14] When applied to **1S-Me** this procedure gives a mixture of four materials, in proportions depending on the nature of the hydrosilane and its concentration. The ^{1}H and ^{13}C NMR spectra of the crude mixture obtained with triethylsilane (TES) (TES : **1S-Me** = 4) indicate that it consists of two (2-anisyl)diadamantylmethanes, in a ratio of about 4 : 1, a trifluoroacetate and a phenol. The last two compounds are the same, **2** and **4**, respectively, as those already identified in the reaction of the alcohol with TFA alone. Chromatographic separation of the products leads to isolation of the anisyldiadamantylmethane mixture, **7-Me**, and of (2-hydroxyphenyl)diadamantylmethane, **4**, in good overall yield. Abandoning the first fraction for several days at room temperature yielded crystals of the minor isomer. A single crystal X-ray diffraction study showed it to have the *anti* conformation, that in which the benzylic hydrogen is remote from the methoxy group.§

The geometry (Table 1, Fig. 1) is typical of aryl- and heteroaryldiadamantylmethyl derivatives,[4,5,12] and is in good agreement with that calculated by molecular mechanics.

The isomeric (2-anisyl)diadamantylmethanes, **7A-Me** and **7S-Me**, are associated with benzylic carbon ^{13}C NMR shifts of 72.3 and 55.3 ppm, respectively. This finding confirms that the differences observed for other aryldiadamantylmethanes[12,15] apply also in the present series.

The carboxonium ion **6** is, therefore, either attacked by nucleophiles to give **2** and **3** or is reduced by hydride transfer from the hydrosilane to give *syn*-(2-anisyl)diadamantylmethane, **7S-Me**. A competing pathway is intermolecular hydride transfer from the hydrosilane to the initially formed carbocation, **5**, leading to *anti*-(2-anisyl)diadamantylmethane, **7A-Me** (Scheme 1). However, we cannot at this stage exclude the possibility that all or part of the *syn* isomer is also the result of direct hydride transfer from the hydrosilane. It should be remarked that in the analogous reaction of (2-alkylphenyl)-diadamantylmethanols intermolecular hydride transfer does not occur,[12] except when sodium borohydride is used.[15] The fact that **7A-Me** is formed at all indicates that the intermolecular/intramolecular rate ratio is higher in the present system.

§ In the past [3,5,12] we have systematically used the same conformational descriptor, *anti* or *syn*, for an alcohol and the alkane obtained by removal of the oxygen atom, despite the fact that OH and H do not have the same priority with respect to carbon. This practice, though incorrect, has the advantage that analogous structures bear the same descriptor, and we shall continue to employ it here.

Table 1 X-Ray crystallographic data for *anti*-(2-anisyl)diadamantylmethane, **7A-Me**. Comparison with MMP2(85)-calculated geometry

	7A-Me[a]	MMP2(85)
Bond lengths/Å		
C(1)–C(10)	1.539(6)	1.539
C(10)–C(101)	1.589(5)	1.576
C(10)–C(201)	1.585(5)	1.579
C(1)–O(1)	1.376(5)	1.371
O(1)–C(7)	1.414(5)	1.414
Bond angles/°		
C(1)–C(10)–C(101)	110.7(3)	112.4
C(1)–C(10)–C(201)	121.5(3)	123.9
C(2)–C(1)–C(10)	126.1(3)	123.1
C(2)–O(1)–C(7)	117.2(3)	117.3
C(1)–C(2)–O(1)	119.4(3)	119.1
Torsion angles/°		
C(2)–C(1)–C(10)–C(101)	−79	−83
C(2)–C(1)–C(10)–C(201)	63	66
C(1)–C(10)–C(101)–C(102)	−171	−165
C(1)–C(10)–C(101)–C(108)	64	70
C(1)–C(10)–C(101)–C(109)	−55	−48
C(1)–C(10)–C(201)–C(202)	139	134
C(1)–C(10)–C(201)–C(208)	24	18
C(1)–C(10)–C(201)–C(209)	−100	−104
C(10)–C(1)–C(2)–O(1)	−5	0
C(1)–C(2)–O(1)C–(7)	170	159

[a] Means of values for two independent molecules.

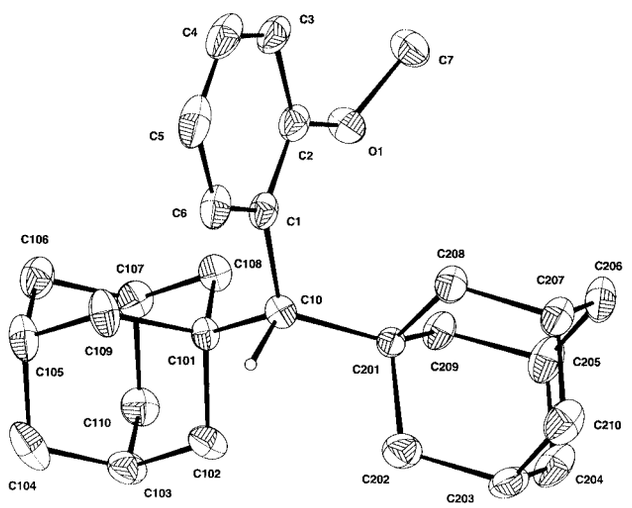


Fig. 1 CAMERON diagram for *anti*-(2-anisyl)di(1-adamantylmethane), **7A-Me**, showing 30% probability displacement ellipsoids. Hydrogen atoms have been omitted for clarity.

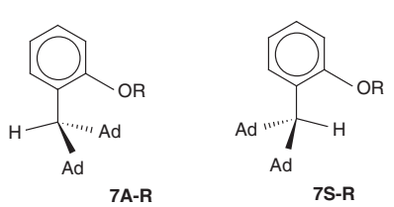
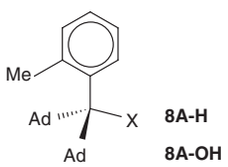


Table 2 Reduction of (2-anisyl)di(1-adamantyl)methanol, **1S-Me**, by TFA–hydrosilane in dichloromethane; initial [ROH] = 0.0183–0.0192; initial [TFA] = 0.48–0.50; estimated [R_3SiH] at one half-life.[a] Rate constants for reaction of hydrosilanes with 4-anisylphenylcarbenium ion at −70 °C (ref. 28)

R_3SiH	[R_3SiH]	**7a-Me**	**7S-Me**	**2**	**4**	%**7A**/(100 − %**7A**)	%**7S**/(%**2** + %**4**)	k_2/dm^3 mol^{-1} s^{-1}
None	—	—	—	91	9	—	—	—
NHS	0.070	12	47	36	5	0.138	1.14	0.048
DPS	0.071	9	45	38	8	0.098	0.99	1.20
TPS	0.072	0	37	49	15	0.0	0.58	8.27
TIPS	0.073	0	28	58	14	0.0	0.40	36.7
TES	0.071	8	41	40	11	0.087	0.82	124
DMPS	0.070	27	34	31	9	0.361	0.86	149
TTMSS	0.072	21	9	54	17	0.259	0.13	457

[a] Data are rounded to the nearest integer %; sum = 100 ± 1%. Ratios calculated before rounding.

Heating the isolated mixture of anisyldiadamantylmethanes for 8 h at 240 °C results in complete conversion to the *syn* isomer, **7S-Me**, the half-life being about 1.5 h at this temperature; this corresponds to an activation energy of around 40 kcal mol^{-1}. Previous work [8] has shown that *anti*-(2-tolyl)diadamantylmethane, **8A-H**, rotates much more slowly than the corresponding alcohol, **8A-OH**, the barrier difference being about 5 kcal mol^{-1}. That of *anti*-(2-anisyl)diadamantylmethanol is expected therefore to be of the order of 35 kcal mol^{-1}, which means that if it were formed it would be isolated as such. The fact that only the *syn* alcohol can be isolated suggests that the stereochemistry of the addition is controlled by attractive interactions between the incipient alcohol oxygen and the methoxy group. The difference between the rotation barriers of *ortho*-tolyl- (*ca.* 45 kcal mol^{-1} at 250 °C)[8] and (2-anisyl)-diadamantylmethanes is consistent with the MM calculations, which indicate that methoxy is less sterically demanding than methyl or ethyl.

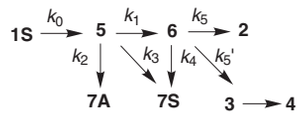


8A-H

8A-OH

(ii) Hydride donor product dependence. A number of hydrosilanes covering a wide range of reactivity [28] and bearing substituents of very different sizes were chosen as hydride donors. Varying the hydride donor (R_3SiH : **1S-Me** = 4) has substantial effects upon the product ratios (Table 2). *n*-Hexylsilane (NHS), TES and diphenylsilane (DPS) give similarly small yields of **7A-Me**, with **2** and **7S-Me** predominating, while in the presence of dimethylphenylsilane (DMPS) the yield of *anti*-anisyldiadamantylmethane, **7A-Me**, is almost as great as that of the *syn* isomer, **7S-Me**. More sterically hindered hydrosilanes such as triphenylsilane (TPS) and tri(isopropyl)silane (TIPS) give no **7A-Me** and modest yields of **7S-Me**, with trifluoroacetate **2** and phenol **4** accounting for about two-thirds of the reaction products. In the case of tris(trimethylsilyl)silane (TTMSS), *anti*-anisyldiadamantylmethane is formed in preference to the *syn* isomer.

These variations in product selectivity clearly depend on differences between the rates of intermolecular hydride transfer and those of intramolecular hydride transfer and nucleophilic attack by trifluoroacetate ion or water on the rearranged cation. The simple kinetic scheme shown in Scheme 2 is an attempt to rationalize these results; the TFA concentration is assumed to be constant and is included in the appropriate rate constants. The question arises as to whether the rate constant for trifluoroacetylation, k_{exp}, corresponds to k_0 or k_1. In fact, the carbocation could be in pre-equilibrium with the alcohol, whereupon the observed rate constant would be Kk_1, where K is a (very small) equilibrium constant. However, the fact that addition of TFAA has little effect upon the rate of reaction of **1S-Me** suggests that the first step is not reversible, *i.e.* that the carbocation is reduced or converted to carboxonium ion as soon as it is formed, and that $k_{exp} = k_0$.



Scheme 2

If direct reaction of **5** to give **7S-Me** is neglected, this scheme suggests that the ratio of *anti*-anisyldiadamantylmethane to all other products, %**7A**/(100 − %**7A**) (the tag "**-Me**" is omitted from all ratios), will be given by k_2[R_3SiH]/k_1, and the ratio of *syn*-anisyldiadamantylmethane to **2** and **4**, %**7S**/(%**2** + %**4**), by k_4[R_3SiH]/(k_5 + $k_{5'}$), where [R_3SiH] is the hydrosilane concentration, assumed to be in sufficiently large excess for it to be treated as constant.

DMPS and TES were chosen for further study. Changing the DMPS concentration leads to significant variations in the product composition (Table 3). If the initial molar ratio of hydrosilane to alcohol is raised from 4 to 16 there is a regular increase in the yield of *anti*-anisyldiadamantylmethane, **7A-Me**, and a decrease in **2** and **4,** with that of **7S-Me** going through a maximum.

Inspection of the resulting values of k_2/k_1 and $k_4/(k_5 + k_{5'})$ obtained by dividing the product ratios by the hydrosilane concentration at one half-life indicates that Scheme 2 is valid for the *anti* isomer but perhaps not for the *syn*; values of k_2/k_1 show only random variations, averaging 5.08 ± 0.17 M^{-1}. Analogous experiments carried out with TES give similar results (Table 3) but with a significantly smaller value for k_2/k_1, 1.18 ± 0.03 M^{-1}. An alternative, rather more rigorous method of calculating k_2/k_1 is to solve the kinetic differential equations by means of a kinetic analysis programme such as KINAL [29] and to use the yields of **7A-Me** and **7S-Me** as targets (see Experimental section), starting with the calculated concentrations of alcohol and hydrosilane. This avoids the approximation involved in assuming that [R_3SiH] is constant and leads to k_2/k_1 values of 5.04 ± 0.15 and 1.17 ± 0.02 M^{-1} for DMPS and TES, respectively, making the ratio of k_2 values (assuming k_1 constant) for DMPS with respect to TES about 4.3.†

Values of k_2/k_1 calculated from the single-concentration experiments for the other hydrosilanes range from zero (TPS and TIPS) to 0.36 M^{-1} (TTMSS) and follow no obvious trend in steric or polar effects. As has been observed in other work on the ionic hydrogenation of aryldi(1-adamantyl)methanols,[15] there is no correlation of the relative rates of reduction of the carbocation with the rates of hydride transfer from these hydrosilanes to diarylcarbenium ions, which are a reflection of almost pure polar effects upon the stability of the incipient silylium ion.[28] The two bulky hydrosilanes, TPS and TIPS, of moderate reactivity do not react at all with the carbocation, whereas the bulky but highly reactive TTMSS does. Steric

Table 3 Hydrosilane concentration and isotope effects on the reduction of (2-anisyl)di(1-adamantyl)methanol, **1S-Me**, by TFA–hydrosilane in dichloromethane; initial [ROH] = 0.0183–0.0192; initial [TFA] = 0.48–0.50; estimated [R_3SiL] at one half-life[a]

R_3SiL	[R_3SiL]	**7A-Me**	**7S-Me**	**2**	**4**	%**7A**/(100 − %**7A**)	%**7S**/(%**2** + %**4**)
TES-*h*	0.071	8	41	40	11	0.087	0.817
TES-*h*	0.144	14	50	28	8	0.167	1.390
TES-*h*	0.216	21	53	21	6	0.258	1.970
TES-*h*	0.286	25	53	18	5	0.333	2.363
TES-*d*	0.145	10	49	33	9	0.112	1.180
TES-*d*	0.216	15	53	25	7	0.179	1.706
TES-*d*	0.286	19	55	21	5	0.233	2.164
DMPS-*h*	0.070	27	34	31	9	0.361	0.863
DMPS-*h*	0.143	43	37	16	4	0.757	1.802
DMPS-*h*	0.215	52	34	11	3	1.062	2.382
DMPS-*h*	0.285	59	31	9	2	1.410	2.879
DMPS-*d*	0.144	31	38	25	6	0.458	1.224
DMPS-*d*	0.216	42	35	20	4	0.721	1.450
DMPS-*d*	0.286	48	33	16	3	0.916	1.757

[a] Data are rounded to the nearest integer %; sum = 100 ± 1%. Ratios calculated before rounding.

effects would appear to be more important in the present reaction than in Mayr's work.[28]

The values of $k_4/(k_5 + k_{5'})$, whether they be obtained simply from the %**7S**/(%**2** + %**4**) ratios or by the KINAL treatment above, tend to decrease as [R_3SiH] increases, by about 20–30% for both hydrosilanes as [R_3SiH]:[**1S-Me**] goes from 4 to 16, average values being 11.7 ± 1.2 and 9.7 ± 1.4 M^{-1} for DMPS and TES, respectively. If an average value is taken for k_2/k_1 and the direct route from **5** to **7S-Me** by hydride transfer to the *syn* face of the carbonium ion is included as only insignificantly small, random values of k_3/k_1 are obtained by KINAL optimization. Comparison of %**7S**/(%**2** + %**4**) ratios for like values of [R_3SiH] indicates that the reactivities of NHS, DPS, DMPS and TES with the carboxonium ion are very similar. The more bulky hydrosilanes, TPS and TIPS give significant amounts of the *syn* isomer, with %**7S**/(%**2** + %**4**) ratios not much less than for the other hydrosilanes. TTMSS is exceptional in that both %**7A**/(100 − %**7A**) and %**7S**/(%**2** + %**4**) are small, the latter being the smaller (Table 3).

The isotope effect study (*vide infra*) confirms the kinetic analysis and shows that *syn*-anisyldiadamantylmethane is formed from the H-shifted cation and not directly from the initially formed cation. However, its rate of formation does not appear to be a simple function of the hydrosilane concentration and/or the rates of formation of **2** and **3** are to some extent [R_3SiH]-dependent. The ratio of trifluoroacetate to phenol, %**2**/%**4**, shows no significant variation with the DMPS or TES concentration, being 3.7 ± 0.3 for the 8 data. Values for the other hydrosilanes range from 3.3 to 6.8. All these values are surprisingly smaller than in the simple reaction of **1S-Me** with TFA, where it is about 9, and the phenol yield is in some cases higher than when no hydrosilane is present. A logical interpretation would be that hydrosilane is involved in the formation of the phenol, but this makes little sense chemically.

The KINAL-Simplex treatment can be extended to include the variation of the water concentration due to its formation from the alcohol and reaction with **6** and possibly with the silylium ion.[30] However, this necessitates the separation of k_5 and $k_{5'}$, and involves the explicit introduction of k_0, k_1 and a rate constant for reaction of silylium ion with water. Rate constant k_0 is known experimentally, the other two and $k_{5'}$ can be set arbitrarily, whereupon k_2, k_4 and k_5 can be optimized. In this way relative rate constants are calculated; they are not very sensitive to the arbitrary values. As far as k_2/k_1 is concerned this treatment gives similar results to the above, 4.98 ± 0.15 and 1.15 ± 0.02 M^{-1} for DMPS and TES, respectively. TES shows the same trend as before for k_4 but not DMPS; as expected, similar values of k_5 are found for the two hydrosilanes.

(iii) Isotope effects. Single electron transfer [SET, eqn. (1)] and synchronous hydride transfer [SHT, eqn. (2)] mechanisms have been proposed for hydride transfers from hydrosilanes to carbocations.

$$R_3SiH + {}^+CR'_3 \rightleftharpoons \underset{\text{encounter complex}}{[R_3SiH\ {}^+CR'_3]} \longrightarrow \underset{\text{free radical pair}}{\{R_3Si^+H\cdot\cdot CR'_3\}} \longrightarrow R_3Si^+ + HCR'_3 \quad (1)$$

$$R_3SiH + {}^+CR'_3 \longrightarrow \underset{\text{transition state}}{[R_3Si\cdots H\cdots CR'_3]^+} \longrightarrow R_3Si^+ + HCR'_3 \quad (2)$$

Arguments in favour of the SET mechanism advanced by Chojnowski *et al.*[31] have been countered by recent work on isotope effects[28] and *ab initio* calculations,[32] which strongly support the SHT process; theory indicates an early, linear transition state for the reaction of CH_3^+ with SiH_4. The recent suggestion that the transition structure of the rate-determining step (in the hydride transfer reaction from arylsilanes to carbocations) is close to the intermediate silyl cations[33] is based on what seems to be an erroneous interpretation of Yukawa–Tsuno r^+ values.

In the ionic hydrogenation of **1S-Me**, replacing DMPS by the silicon-deuteriated compound, Me_2PhSiD, has relatively small effects on the product composition, the most notable change being a decrease in the amount of *anti*-(2-anisyl)diadamantylmethane, **7A-Me**, and an increase in trifluoroacetate, **2** (Table 3). NMR study of the product mixture shows no benzylic CH proton signal for this compound and a very weak triplet in the ^{13}C spectrum. The *syn* isomer, **7S-Me**, on the other hand has normal CH signals but the methyl signals are replaced by triplets slightly upfield from the usual values: 55.4 ppm (J = 22 Hz) for carbon and 3.77 ppm (J = 1.5 Hz) for proton. The spectra of the trifluoroacetate **2** and phenol **4** are perfectly normal. These results are consistent with the mechanism outlined above, and establish that *syn*-(2-anisyl)diadamantylmethane, **7S-Me**, is formed by reduction of a H-shifted carbocation, *i.e.* the carboxonium ion, **6**.

Calculation of the kinetic isotope effects (KIE) from the product composition, individual values of the %**7A**/(100 − %**7A**) ratio for each DMPS concentration being used, leads to a small value for the KIE on k_2, 1.55 ± 0.09 at room temperature (20 ± 2 °C). This is similar to values reported by Chojnowski[31] at 25 °C and considered by him to be secondary isotope effects supporting the SET mechanism. However, Mayr has shown that small isotope effects are consistent with rate-determining Si–H cleavage.[28] It is more difficult to say anything about the effects on the reduction of the carboxonium ion, since the kinetic analysis is less satisfactory. Point-by-point comparisons

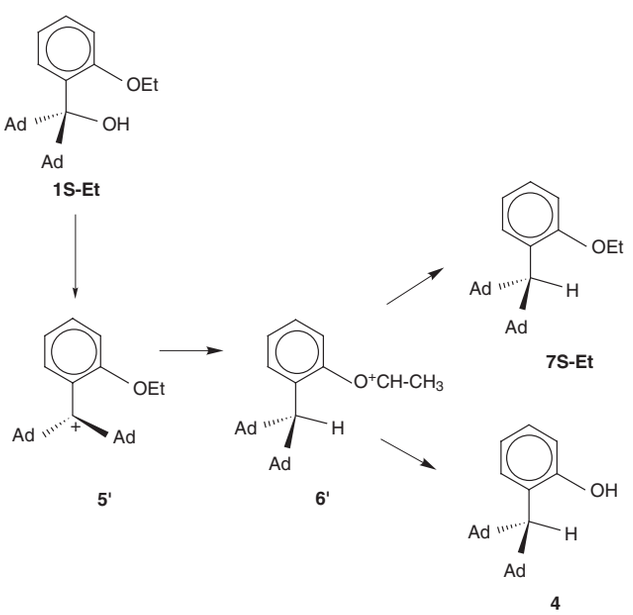
Table 4 Reduction of (2-ethoxyphenyl)di(1-adamantyl)methanol, **1S-Et**, by TFA–hydrosilane in dichloromethane; initial [ROH] 0.0183–0.0192; initial [TFA] 0.48–0.50; estimated [R_3SiL] at one half-life.[a] Rate constants for reaction of hydrosilanes with 4-anisylphenylcarbenium ion at −70 °C (ref. 28)

R_3SiL	[R_3SiL]	**4**	**7S-Et**	%**7S-Et**/%**4**	k_2/dm^3 mol^{-1} s^{-1}	KIE
None	—	100	0			
NHS-*h*	0.076	97	3	0.032	0.048	
DPS-*h*	0.075	85	15	0.179	1.20	
TPS-*h*	0.073	78	22	0.283	8.27	
TIPS-*h*	0.072	60	40	0.658	36.7	
TES-*h*	0.069	27	73	2.76	124	
TES-*d*	0.070	31	69	2.27		1.22
TES-*h*	0.143	15	85	5.56		
TES-*d*	0.143	19	81	4.24		1.31
TES-*h*	0.214	12	88	7.44		
DMPS-*h*	0.070	33	67	2.07	149	
DMPS-*d*	0.070	39	61	1.54		1.35
DMPS-*h*	0.143	17	83	5.00		
DMPS-*d*	0.143	22	78	3.65		1.37
DMPS-*h*	0.215	12	88	7.52		
DMPS-*d*	0.215	16	84	5.21		1.44
DMPS-*h*	0.285	10	90	9.26		
TTMSS-*h*	0.072	61	39	0.63	457	

[a] Data are rounded to the nearest integer %; sum = 100 ± 1%. Ratios calculated before rounding.

give a similar value, 1.58 ± 0.10, which must correspond essentially to the KIE on k_4. The value for the isotope effect on k_2 when TES is replaced by Et_3SiD is 1.45 ± 0.03, which is in fair agreement with the value for DMPS, but the effect on k_4 is unexpectedly small, 1.14 ± 0.05. We have no explanation for this difference nor for such a small value. Treatment of the data by KINAL in its reduced or more elaborate form does not give significantly different results.

***syn*-(2-Ethoxyphenyl)di(1-adamantyl)methanol.** Reaction of alcohol **1S-Et** with TFA in the presence of a hydrosilane is much simpler than that of **1S-Me** in that it gives only the phenol, **4**, and *syn*-(2-ethoxyphenyl)diadamantylmethane, **7S-Et** (Scheme 3). Using a 16-fold excess of the most reactive



Scheme 3

hydrosilane, DMPS, serves only to reduce the phenol yield. This shows clearly that the relative rate of intramolecular hydride shift to intermolecular hydride transfer from a hydrosilane is much greater for the ethoxy group than for methoxy. This is perfectly reasonable insofar as the primary carboxonium ion **6′** bears a methyl substituent on the formally charged carbon, and this must enhance its stability. Conversely, there is no evidence for nucleophilic attack by trifluoroacetate ion nor for formation of a 1-phenoxyethanol analogue of **3**. Instead, the carboxonium ion eliminates acetaldehyde, presumably by reaction with water, to give phenol **4** directly.

Variation of the nature and the concentration of the hydrosilane (Table 4) gives results differing qualitatively from those for **1S-Me**. With a four-fold ratio of hydrosilane to alcohol, the three least reactive hydrosilanes, according to Mayr's classification,[28] NHS, DPS and TPS, give the smallest amounts of **7S-Et** while the most reactive, TTMSS, gives similar amounts of **7S-Et** and **4**, as does TIPS. TES and DMPS favour **7S-Et** relative to **4**. Leaving aside TTMSS, which gives far too little deoxygenation product, there is a rough correlation of the %**7S-Et**/%**4** ratio with Mayr's rate constants[28] for reaction with a diarylcarbonium ion, TES and DMPS, however, being reversed. The slope of the correlation is, nevertheless, small (1.5–2%) and suggests that if the polar effects of the hydrosilane substituents do affect k_4 (Scheme 2) they are still of minor importance. What is remarkable is that such a correlation should exist at all for **1S-Et** when the corresponding rate constant for **1S-Me** appears to be controlled primarily by steric effects.

By analogy with Scheme 2 we can reasonably expect that the ratio of **7S-Et** to **4** will be given by k_4[R_3SiH]/$k_{5'}$, in which case %**7S-Et**/%**4** should be a linear function of [R_3SiH], with the assumptions stated above. In the case of DMPS a point-by-point evaluation of $k_4/k_{5'}$ gives an average of 33.1 ± 2.6 M^{-1}. Again, a better method of calculating $k_4/k_{5'}$ is by means of KINAL[29] using the yields of **7S-Et** as targets. This gives an average value of 33.2 ± 2.5 M^{-1}, in good agreement with the first estimate. The same procedure applied to the three data for normal TES gives a slightly higher value, 38.0 ± 2.8 M^{-1}. As with **1S-Me**, TES and DMPS react at similar rates with the carboxonium ion. If $k_4/k_{5'}$ is calculated from the %**7S-Me**/%**4** ratios for reaction of **1S-Me**, there is considerable scatter but no well defined trend in the values, giving 44.1 ± 5.7 and 54.5 ± 4.9 M^{-1} for TES and DMPS, respectively. These values are not very different from those obtained for **1S-Et**, which shows that the relative rates of reduction and reaction with water are similar for the two carboxonium ions. The major difference is that **6′** does not react with trifluoroacetate.

Kinetic isotope effects on k_4 should be more reliable in this system, given that there are only two products rather than four in the previous case. Calculating for each pair of experiments at the same hydrosilane:alcohol ratio (Table 4) gives values slightly higher for DMPS (average 1.39 ± 0.05) than for TES

(1.26 ± 0.07, 2 points only). However, given the uncertainty on the product ratios, even here the individual KIE values carry an uncertainty of about ± 0.1. Neither the apparent variation of the KIE with increasing DMPS concentration nor the difference between TES and DMPS can be considered as significant.

Conclusion

Intramolecularly hydrogen-bonded alcohols are obtained by *ortho*-lithiation of alkoxybenzenes followed by reaction with di(1-adamantyl) ketone. When a carbocation is formed from the methoxy derivative, **1S-Me**, in TFA–dichloromethane, it is rapidly converted to a carboxonium ion by intramolecular 1,5-hydride transfer and thence to a trifluoroacetate and a phenoxymethanol derivative. If a hydrosilane is added in order to trap either or both of the cations by intermolecular hydride transfer, trifluoroacetate formation remains of major importance. The product data show that intra- and intermolecular hydride transfer proceed at similar rates. The variation of the product distribution with the nature and the concentration of the hydrosilane can be understood in terms of a partition of the carbocation and the carboxonium ion between pathways which are [R_3SiH]-dependent or not. The *anti*- and *syn*-(2-anisyl)-diadamantylmethanes, **7A-Me** and **7S-Me**, are formed exclusively by reduction of the carbocation and the carboxonium ion, respectively. Kinetic deuterium isotope effects on the reaction of the carbocation are normal, but the behaviour of the carboxonium ion appears inconsistent. Certain aspects of the reactivity of the carboxonium ion are anomalous; this may be due to the relative imprecision of the data or, possibly, the effects of organosilane species arising from reactions of the silylium ion. Intramolecular hydride transfer is much faster for the (2-ethoxyphenyl) analogue, **1S-Et**, and neither trifluoroacetate nor *anti*-(2-ethoxyphenyl)diadamantylmethane is formed.

Experimental

General methods

NMR measurements were performed on a Bruker AS 200 FT instrument operating at 200 MHz (proton) or 50 MHz (carbon). Chemical shifts are given in ppm and *J* values in Hz. Measurements were made in hexadeuteriobenzene, deuteriochloroform, pentadeuteriopyridine, hexadeuteriodimethyl sulfoxide or dichlorodideuteriomethane (reference values: δ_H = 7.16, 7.26, 8.71, 2.50 and 5.32 ppm for ^1H; δ_C = 128.0, 77.0, 149.9, 39.5 and 53.8 ppm). Carbon and hydrogen shifts of the aromatic system are numbered: C2, C3, *etc*. Generally, the proton signals were assigned on the basis of shifts, coupling constants[34] and spectrum simulation by the gNMR program (Cherwell Scientific).[35] The corresponding ^{13}C signals were identified by heteronuclear correlation experiments. IR spectra were measured in carbon tetrachloride on a Nicolet Magna 860 FTIR spectrometer with 1 cm^{-1} resolution. GC/MS measurements were performed on a CP-Sil 5 capillary column coupled to a Finnigan MAT ITD 800B Ion Trap Detector with chemical ionization (isobutane). Gas chromatography was performed on a 30 cm 10% SE30 on Chrompack column. Column chromatography was performed on silica gel 60 (Merck) in light petroleum (boiling range 35–60 °C)–dichloromethane mixtures or on alumina (Merck, Brockmann III) in light petroleum–diethyl ether mixtures. Melting points were determined in capillary glass tubes on a Mettler FP5 instrument with a heating rate of 3 °C min^{-1}.

Alcohol synthesis

***syn*-(2-Anisyl)di(1-adamantyl)methanol, 1S-Me.** To a solution of anisole (0.54 cm^3, 0.54 g, 5 mmol) and TMEDA (0.75 cm^3, 5 mmol) in sodium–dry diethyl ether (15 cm^3) stirred at room temperature under argon was added a solution of *n*-butyllithium in hexane (1.6 M, 3 cm^3, 4.8 mmol). After 1 h a solution of di(1-adamantyl) ketone (0.153 g, 0.5 mmol) in diethyl ether (20 cm^3) was added in about 10 min. The reaction mixture was stirred at room temperature overnight, then quenched with water and the organic material extracted with hexane, washed with water, dried ($MgSO_4$) and purified on silica gel to give the required alcohol which crystallized with one molecule of dichloromethane for two molecules of alcohol (0.206 g, 89%), **1S-Me**: mp 202 °C (dichloromethane–hexane); ν_{OH}/cm^{-1} (CCl_4) 3499; δ_C (chloroform) 29.4 (6 CH), 37.1 (6 CH_2), 39.2 (6 CH_2), 46.4 (2 C_q), 57.5 (CH_3), 87.2 (OH), 114.3 (C3), 119.4 (C5), 126.9 (C4), 131.2 (C6), 131.3 (C1) and 159.0 (C2); δ_H (chloroform) 1.60–2.0 (br m, Ad), 3.87 (CH_3), 6.58 (OH, constant for 0.00013–0.13 M), 6.94 (H5, *J* 1.4, 7.2 and 8.1), 6.95 (H3, *J* 0.3, 1.4 and 8.3), 7.20 (H4, *J* 1.7, 7.2 and 8.3) and 7.57 (H6, *J* 0.3, 1.7 and 8.1); δ_H(OH) 6.74, 6.53 and 6.80 ppm in C_6D_6, DMSO-d_6 and C_5D_5N, respectively; $\Delta\delta/\delta T = -1.60 \pm 0.04$ ppb $°C^{-1}$ in the last solvent (Found: C, 76.5; H, 8.9; Cl, 7.2. $C_{28}H_{38}O_2{\cdot}0.5CH_2Cl_2$ requires C, 76.23; H, 8.75; Cl, 7.89%).

An alternative procedure was to run the lithiation in THF (10 cm^3), adding the ketone (0.30 g, 1.0 mmol) in THF (15 cm^3) after about 25 min. The reaction was complete in less than 1 h, and chromatography on alumina gave the alcohol (free of dichloromethane) in 91% yield, mp 202.5 °C.

***syn*-(2-Ethoxyphenyl)di(1-adamantyl)methanol, 1S-Et.** As for **1S-Me**, reaction of phenetole with *n*-butyllithium in THF in the presence of TMEDA, followed by reaction with diadamantyl ketone, gave the required alcohol (73%): mp 194 °C (hexane); ν_{OH}/cm^{-1} (CCl_4) 3480; δ_C (chloroform) 15.1 (CH_3), 29.4 (6 CH), 37.2 (6 CH_2), 39.3 (6 CH_2), 46.4 (2 C_q), 66.7 (CH_2), 87.4 (OH), 115.3 (C3), 119.4 (C5), 126.9 (C4), 131.4 (C6), 131.5 (C1) and 158.3 (C2); δ_H (chloroform) 1.46 (CH_3, *J* 7.0), 1.60–2.0 (br m, Ad), 4.11 (CH_2, *J* 7.0), 6.79 (OH), 6.92 (H5, *J* 1.4, 7.2 and 8.1), 6.93 (H3, *J* 0.3, 1.4 and 8.3), 7.17 (H4, *J* 1.7, 7.2 and 8.3) and 7.57 (H6, *J* 0.3, 1.7 and 8.1); δ_H(OH) 6.99, 6.72 and 7.05 ppm in C_6D_6, DMSO-d_6 and C_5D_5N, respectively; $\Delta\delta/\delta T = -1.59 \pm 0.02$ ppb $°C^{-1}$ in the last solvent (Found: C, 82.7; H, 9.8. $C_{29}H_{40}O_2$ requires C, 82.81; H, 9.58%).

Reactions with TFA

***syn*-(2-Anisyl)di(1-adamantyl)methanol, 1S-Me.** *NMR study.* To the alcohol (12 mg, 0.03 mmol) and deuteriated dichloromethane (0.5 cm^3) in an NMR tube was added TFA (0.02 cm^3). The mixture was briefly shaken and the tube replaced in the NMR apparatus at 25 °C. The ^1H spectrum was recorded at intervals over a period of about 1 h, corresponding to about 3 half-lives of the reaction. Signals at 6.00 and 2.86 ppm, shown by correlation with the ^{13}C spectrum to correspond to CH_2 and benzylic CH groups, respectively, appeared progressively at the expense of the methyl signal (3.94 ppm) of the alcohol. These new signals were attributed to a trifluoroacetate, **2**. An "infinity" sample taken after *ca*. 10 half-lives showed 90% conversion to the trifluoroacetate, **2**, and about 10% of a material revealed by small signals at 5.46 (CH_2) and 2.41 (CH) ppm, correlated with ^{13}C signals at 67.7 and 58.8 ppm, respectively. Only three aromatic CH carbons could be located (117.8, 128.7 and 133.3 ppm) and two quaternary carbons (129.7 and 153.4 ppm). This product was tentatively identified as *syn*-2-[di(1-adamantyl)-methyl]phenoxymethanol, **3**.

A first-order rate constant was estimated by integration of the CH_2 and CH_3 signals, the solvent $CHDCl_2$ peak being used as an internal standard. Plotting log $(CH_3)_t$ or log $[(CH_2)_\infty - (CH_2)_t]$ *vs.* time (*t*) gave a good straight line over two-half lives corresponding to a first-order rate constant of $7.15 \pm 0.14 \times 10^{-4}$ s^{-1} (4 runs). Prior addition of trifluoroacetic anhydride (0.02 cm^3) to the reaction mixture gave an auto-

catalytic reaction with an inital rate constant (one half-life) of $7.2 \pm 0.5\ s^{-1}$.

Aqueous work-up. Alcohol **1S-Me** (100 mg, 0.25 mmol) was treated with TFA (0.5 cm^3) in dichloromethane (10 cm^3) at room temperature for 3 h and then quenched in a mixture of water and pentane. The organic layer was twice washed with water, then dried ($MgSO_4$) and the solvents evaporated. NMR analysis of the residue indicated a 9:1 mixture of trifluoroacetate, **2**, and a phenol, **4**. Chromatography on silica gave the phenol (85 mg; 82%). Attempts to crystallize the trifluoroacetate were unsuccessful.

syn-[2-(α-Trifluoroacetylanisyl)]di(1-adamantyl)methane, ***2***: δ_C (chloroform) 29.2 (6 CH), 37.0 (6 CH_2), 39.1 (2 C_q), 42.9 (6 CH_2), 56.1 (CH), 89.4 (CH_2), 113.4 (C3), 114.3 (CF_3, *J* 286 Hz), 121.9 (C5), 126.5 (C4), 131.9 (C6), 132.6 (C1), 155.3 (C2) and 156.6 (C=O, *J* 43 Hz); δ_H (chloroform) 1.5–2.0 (br m, Ad), 2.84 (CH), 6.00 (CH_2), 7.04 (H3, *J* 0.4, 1.2 and 8.2), 7.06 (H5, *J* 1.2, 7.4 and 7.8), 7.20 (H4, *J* 1.7, 7.4 and 8.2) and 7.42 (H6, *J* 0.4, 1.7 and 7.8); *m*/*z* (ITD) 501 (M − 1, 4%), 389, 387, 366, 253, 251, 136, 135 (100%), 107, 93, 79.

syn-(2-Hydroxyphenyl)di(1-adamantyl)methane, ***4***: mp 223 °C (dichloromethane–hexane); ν_{OH}/cm^{-1} (CCl_4) 3609; δ_C (chloroform) 29.2 (6 CH), 37.0 (6 CH_2), 39.4 (2 C_q), 43.0 (6 CH_2), 57.2 (CH), 115.0 (C3), 119.1 (C5), 126.1 (C4), 128.6 (C1), 131.4 (C6) and 154.1 (C2); δ_H (chloroform) 1.5–2.0 (br m, Ad), 2.57 (CH), 4.64 (OH), 6.76 (H3, *J* 0.1, 1.3 and 8.0), 6.86 (H5, *J* 1.3, 7.3 and 7.8), 7.06 (H4, *J* 1.7, 7.3 and 8.0) and 7.33 (H6, *J* 0.1, 1.7 and 7.8); *m*/*z* (ITD) 376 (M, 7%), 375, 240, 239, 136, 135 (100%), 107, 93, 79 (Found: C, 79.2; H, 8.8; Cl, 8.0. $C_{27}H_{36}O{\cdot}0.5CH_2Cl_2$ requires C, 78.82; H, 8.90; Cl, 8.46%).

Reactions with TFA

***syn*-(2-Ethoxyphenyl)di(1-adamantyl)methanol, 1S-Et. NMR study.** As for **1S-Me**, to the alcohol (12 mg, 0.03 mmol) and deuteriated dichloromethane (0.5 cm^3) in an NMR tube was added TFA (0.02 cm^3). The mixture was briefly shaken and the tube replaced in the NMR apparatus at 25 °C. The ^1H NMR spectrum recorded over about 30 min showed progressive disappearance of the ethyl group signals at 1.44 and 4.10 ppm and modifications in the aromatic part of the spectrum. A well defined doublet (*J* = 3.0 Hz) at 2.34 ppm coupled with a quadruplet at 9.75 ppm was attributed to the formation of acetaldehyde. The ^{13}C NMR spectrum of the mixture, taken 5–15 hours after mixing, was identical with that of phenol, **4**, under the same conditions.

Ionic hydrogenation

***syn*-(2-Anisyl)di(1-adamantyl)methanol, 1S-Me.** *Preparative experiments.* (i) Treatment of alcohol **1S-Me** (150 mg, 0.37 mmol) in dichloromethane (15 cm^3) with TES (0.2 cm^3, 1.25 mmol) and TFA (0.75 cm^3) at room temperature for 1 h gave a 4:4:1:1 four-component mixture. The major components were identified as *syn*-(2-anisyl)di(1-adamantyl)methane, **7S-Me**, and the trifluoroacetate, **2**. The minor components, identified and characterized in subsequent experiments, proved to be *anti*-(2-anisyl)di(1-adamantyl)methane, **7A-Me**, and the phenol, **4**. Separation of the less polar from the more polar materials by chromatography on silica gel gave a mixture of **7A-Me** and **7S-Me** (74 mg, 49%) and the phenol, **4** (68 mg, 47%).

(ii) Treatment of alcohol **1S-Me** (100 mg, 0.25 mmol) in dichloromethane (10 cm^3) with TES (1 cm^3, 6.3 mmol) and TFA (0.25 cm^3) at room temperature for 40 h gave a mixture of **7S-Me**, **7A-Me** and trifluoroacetate, **2**, in a ratio of 4:4:1 with traces of the phenol. Chromatographic separation gave a mixture of **7A-Me** and **7S-Me** (78 mg, 81%), followed by phenol, **4** (9 mg, 10%). Heating the mixture of **7A-Me** and **7S-Me** in chloroform for 8 h at 240 °C resulted in complete conversion to **7S-Me**, confirming that this is the more stable, *syn* isomer. The half-life was estimated to be 1.5 h at this temperature.

anti-(2-Anisyl)di(1-adamantyl)methane, ***7A-Me***: mp 148 °C (crystallized from a mixture of **7A-Me** and **7S-Me** on standing for several days, pentane-washed); δ_C (chloroform) 29.6 (6 CH), 37.2 (6 CH_2), 38.9 (2 C_q), 43.5 (6 CH_2), 53.8 (CH_3), 72.3 (CH), 110.7 (C3), 119.3 (C5), 126.9 (C4), 131.1 (C1), 136.6 (C6) and 157.9 (C2); δ_H (chloroform) 1.5–2.0 (br m, Ad), 2.05 (CH), 3.80 (CH_3), 6.81 (H5, *J* 1.2, 7.3 and 7.4), 6.87 (H3, *J* 0.6, 1.2 and 8.2), 6.97 (H6, *J* 0.6, 1.8 and 7.4) and 7.19 (H4, *J* 1.8, 7.3 and 8.2) (Found: C, 86.2; H, 9.9. $C_{28}H_{38}O$ requires C, 86.10; H, 9.81%).

syn-(2-Anisyl)di(1-adamantyl)methane, ***7S-Me***: mp 200 °C (crystallized from another mixture of **7A-Me** and **7S-Me**, pentane-washed); δ_C (chloroform) 29.3 (6 CH), 37.1 (6 CH_2), 39.1 (2 C_q), 42.9 (6 CH_2), 55.3 (CH), 55.7 (CH_3), 110.4 (C3), 118.7 (C5), 125.9 (C4), 131.1 (C6), 131.4 (C1) and 158.5 (C2); δ_H (chloroform) 1.5–2.0 (br m, Ad), 2.97 (CH), 3.80 (CH_3), 6.86 (H3, *J* 0.5, 1.1 and 8.1), 6.89 (H5, *J* 1.1, 7.4 and 7.7), 7.17 (H4, *J* 1.7, 7.4 and 8.1) and 7.35 (H6, *J* 0.5, 1.7 and 7.7) (Found: C, 86.1; H, 9.6. $C_{28}H_{38}O$ requires C, 86.10; H, 9.81%).

Small-scale experiments. To a stirred solution of alcohol **1S-Me** (40 mg, 0.1 mmol) and a hydrosilane (0.15–2.4 mmol) in dichloromethane (5 cm^3) at room temperature (20 ± 2 °C) was added TFA (0.2 cm^3). After 3 h water and pentane were added, the pentane extract washed twice with water, then dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The residue was taken up in deuteriochloroform for ^{13}C NMR analysis, the aromatic and benzylic CH signals being used to estimate the relative yields (± 2%, *i.e. x*% means *x* ± 2% except for the smallest values where the uncertainty is ± 1%) of the four products identified above. No significant amount of any other material was detected. The hydrosilane concentrations were calculated on the assumption that dichloromethane, TFA and hydrosilane volumes are additive; values given in Tables are for one half-life of the alcohol, based on the calculated uptake of hydrosilane to give **7A-Me** and **7S-Me**.

***syn*-(2-Ethoxyphenyl)di(1-adamantyl)methanol, 1S-Et**. *Preparative experiment.* Treatment of alcohol **1S-Et** (114 mg, 0. 27 mmol) in dichloromethane (10 cm^3) with TES (0.15 cm^3, 0.7 mmol) and TFA (0.5 cm^3) at room temperature for 1 h gave *syn*-(2-ethoxyphenyl)di(1-adamantyl)methane, **7S-Et**, together with a smaller amount (*ca.* 40%) of phenol, **4**. No other products were detected. Chromatographic separation gave **7S-Et** (60 mg, 55%) and **4** (29 mg, 28%).

syn-(2-Ethoxyphenyl)di(1-adamantyl)methane, ***7S-Et***: mp 171 °C (hexane); δ_C (chloroform) 15.2 (CH_3), 29.3 (6 CH), 37.1 (6 CH_2), 39.0 (2 C_q), 42.9 (6 CH_2), 55.2 (CH), 63.6 (CH_2), 111.2 (C3), 118.4 (C5), 125.8 (C4), 131.1 (C6), 131.5 (C1) and 157.8 (C2); δ_H (chloroform) 1.43 (CH_3, *J* 7.0), 1.5–2.0 (br m, Ad), 3.03 (CH), 4.01 (CH_2, *J* 7.0), 6.84 (H3, *J* 0.4, 1.2 and 8.1), 6.87 (H5, *J* 1.2, 7.3 and 7.7), 7.14 (H4, *J* 1.7, 7.3 and 8.1) and 7.35 (H6, *J* 0.4, 1.7 and 7.7) (Found: C, 86.0; H, 9.9. $C_{29}H_{40}O$ requires C, 86.08; H, 9.96%).

Isotope effects. Triethylsilane-*d* and dimethylphenylsilane-*d* were prepared by the reduction of the corresponding silyl chlorides by lithium aluminium deuteride in diethyl ether at reflux.[36] Small-scale experiments were carried out as described above. The only important changes in the NMR spectra were as follows: for *anti*-(2-anisyl)diadamantylmethane, **7A-Me**, loss of benzylic proton signal and replacement of corresponding carbon signal by a weak triplet at 71.7 ppm (*J* = 18 Hz); for *syn*-(2-anisyl)diadamantylmethane, **7S-Me**, replacement of methyl signals by triplets slightly upfield from the usual values: 55.4 ppm (*J* = 22 Hz) for carbon and 3.77 ppm (*J* = 1.5 Hz) for proton; **7S-Et**, replacement of CH_2 carbon signals by triplet slightly upfield from the usual value: 63.3 ppm (*J* = 22 Hz). The CHD proton signal is a slightly broadened quartet at 3.98 ppm (*J* = 6.9 Hz) and the CH_3 signal a doublet at 1.41 ppm (*J* = 6.9 Hz).

Molecular mechanics calculations

Steric energies and geometries were calculated with Allinger's MM2(85) force field.[18] The alcohol and deoxygenation product rotamers give the following steric energies: **1S-Me**, 63.17; **1A-Me**, 64.98; **7S-Me**, 50.79; **7A-Me**, 52.90 kcal mol^{-1}. To estimate the steric energies of the phenol rotamers it was necessary to introduce parameters for a type 2–6–21 bond angle; it was taken as equivalent to type 1–6–21; values were 47.04 (**4S**) and 49.46 (**4A**) kcal mol^{-1}. Inclusion of the phenolic oxygen in the π-electron system reduced these values by about 0.1 kcal mol^{-1}.

Kinetic modelling

In KINAL[29] the solution of kinetic differential equations is based on a fourth-order semi-implicit Runge–Kutta method. In our hands it is associated with a Simplex routine, making it possible to optimize a number of rate constants by matching experimental yields ("targets") with those calculated. Since the number of targets is almost invariably smaller than the number of rate constants in the system, certain rate constants are given arbitrary values. Normally, the relative rate constants are insensitive to these values. For calculations involving water it was assumed that the initial concentration of water in dichloromethane was the upper limit indicated for this reagent (ACS grade, ≤0.2%).

X-Ray crystallography

***anti*-(2-Anisyl)di(1-adamantylmethane), 7A-Me: $C_{28}H_{38}O$.** *Crystal data.*¶ $M = 390.6$. Monoclinic $a = 10.945(8)$, $b = 25.069(11)$, $c = 16.530(10)$ Å, $\beta = 104.71(5)$, $V = 4387(5)$ $Å^3$ (by least squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.71069$ Å), space group $P2_1/n$, $Z = 8$, $D_x = 1.18$ g cm^{-3}. The asymmetric unit contains two independent molecules. Colourless prismatic crystals, μ(Mo-Kα) = 0.64 cm^{-1}.

Data collection and processing. Enraf-Nonius CAD4 diffractometer, $\omega/2\theta$ mode with ω scan width = 0.8 + 0.345 tan θ, graphite-monochromated Mo-Kα radiation. 8342 reflections measured ($1 \leq \theta \leq 25°$), 7699 unique, giving 3523 with $I > 3\sigma(I)$.

Structure analysis and refinement. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic; hydrogens located from Fourier difference map with one, overall, refined isotropic thermal parameter (524 refinable parameters). No absorption correction. Final R and R_w (Chebyshev series) values are 0.051 and 0.064. Program used is the PC version of CRYSTALS[37] for refinements and CAMERON[38] for views.

Acknowledgements

We are indebted to Ms Claude Charvy for the GC-MS studies, to Dr A. Adenier for IR measurements and to Drs M. Hedayatullah and J-M. El Hage Chahine for helpful discussions. We thank Dr T. Turányi for access to KINAL and P. Levoir for help in programming the Simplex version.

¶ CCDC reference number 188/171. See http://www.rsc.org/suppdata/p2/1999/1639 for crystallographic files in .cif format.

References

1 R. C. Fort, *Adamantane: the Chemistry of Diamond Molecules*, Marcel Dekker, New York, 1976.
2 J. S. Lomas and J. E. Dubois, *Tetrahedron*, 1981, **37**, 2273.
3 (*a*) J. S. Lomas, P. K. Luong and J. E. Dubois, *J. Org. Chem.*, 1977, **42**, 3394; (*b*) J. S. Lomas and V. Bru-Capdeville, *J. Chem. Soc., Perkin Trans. 2*, 1994, 459.
4 J. S. Lomas and J. Vaissermann, *Bull. Soc. Chim. Fr.*, 1996, **133**, 25; J. Vaissermann and J. S. Lomas, *Acta Crystallogr., Sect. C*, 1997, **53**, 1341.
5 J. S. Lomas and J. Vaissermann, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1777.
6 A. G. Davies and A. G. Neville, *J. Chem. Soc., Perkin Trans. 2*, 1991, 2021.
7 G. A. Olah, G. K. S. Prakash and R. Krishnamurti, *J. Am. Chem. Soc.*, 1990, **112**, 6422.
8 J. S. Lomas and J. E. Anderson, *J. Org. Chem.*, 1995, **60**, 3246.
9 J. S. Lomas, *J. Chem. Soc., Perkin Trans. 2*, 1996, 2601.
10 G. A. Olah, M. D. Heagy and G. K. S. Prakash, *J. Org. Chem.*, 1993, **58**, 4851; M. D. Heagy, G. A. Olah, G. K. S. Prakash and J. S. Lomas, *J. Org. Chem.*, 1995, **60**, 7355.
11 J. S. Lomas, A. Adenier, C. Cordier and J. C. Lacroix, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2647.
12 J. S. Lomas and J. Vaissermann, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1831.
13 R. A. Rennels, A. J. Maliakal and D. B. Collum, *J. Am. Chem. Soc.*, 1998, **120**, 421 and references therein.
14 D. N. Kursanov, Z. N. Parnes and N. M. Loim, *Synthesis*, 1974, 633; I. Fleming, *Organic Silicon Chemistry* in *Comprehensive Organic Chemistry*, ed. D. Barton and W. D. Ollis, Pergamon Press, Oxford, 1979, vol. 3, p. 541; Y. Nagai, *Org. Prep. Proced. Int.*, 1980, **12**, 13; W. P. Weber, *Silicon Reagents for Organic Synthesis*, Springer-Verlag, Berlin-Heidelberg, 1983, p. 273; E. W. Colvin, *Silicon Reagents in Organic Synthesis*, Academic Press, London, 1988; E. Keinan, *Pure Appl. Chem.*, 1989, **61**, 1737; G. L. Larson in *The Chemistry of Organosilicon Compounds*, ed. S. Patai and Z. Rappoport, Wiley Interscience, Chichester, 1989, Part 1, ch. 11, p. 776.
15 J. S. Lomas and J. Vaissermann, *J. Chem. Soc., Perkin Trans. 2*, 1997, 2589.
16 H. W. Gschwend and H. R. Rodriguez, *Org. React.* (*N.Y.*), 1979, **26**, 1.
17 M. Ito and M. Hirota, *Bull. Soc. Chem. Jpn.*, 1981, **54**, 2093.
18 N. L. Allinger, *Quantum Chemistry Program Exchange*, Program MMP2(85), Indiana University, USA.
19 J. Vaissermann, unpublished results.
20 R. Taylor and O. Kennard, *Acc. Chem. Res.*, 1984, **17**, 320.
21 T. Ohishi, J. Yamada, Y. Inui, T. Sakaguchi and M. Yamashita, *J. Org. Chem.*, 1994, **59**, 7521.
22 K. Pihlaja and A. Lampi, *Acta. Chem. Scand., Ser. B*, 1986, **40**, 196.
23 (*a*) H. Perst, *Oxonium Ions in Organic Chemistry*, Verlag Chemie, Weinheim, 1971; (*b*) G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 767 and references therein.
24 J. L. Fry and G. J. Karabatsos, in *Carbonium Ions*, ed. G. A. Olah and P. v. R. Schleyer, Wiley-Interscience, New York, vol. II, 1970, ch. 14.
25 R. A. McClelland, *Can. J. Chem.*, 1975, **53**, 2763.
26 J. K. Pau, J. K. Kim and M. C. Caserio, *J. Am. Chem. Soc.*, 1978, **100**, 3838, 4242.
27 U. R. Ghatak, B. Sanyal, S. Ghosh, M. Sarkar, M. S. Raju and E. Wenkert, *J. Org. Chem.*, 1980, **45**, 1081.
28 H. Mayr, N. Basso and G. Hagen, *J. Am. Chem. Soc.*, 1992, **114**, 3060.
29 T. Turányi, *Comput. Chem.*, 1990, **14**, 253. T. Turányi, *New. J. Chem.*, 1990, **14**, 795.
30 For recent contributions to the silylium ion debate, see: S. H. Strauss, *Chemtracts: Inorg. Chem.*, 1993, **5**, 119; J. B. Lambert, S. Zhang and S. M. Ciro, *Organometallics*, 1994, **13**, 2430; J. B. Lambert and S. Zhang, *Science*, 1994, **263**, 984; G. A. Olah, G. Rasul, X. Li, H. A. Buchholz, G. Sandford and G. K. S. Prakash, *Science*, 1994, **263**, 983; L. Pauling, *Science*, 1994, **263**, 983; C. A. Reed and Z. Xie, *Science*, 1994, **263**, 985; J. B. Lambert, L. Kania and S. Zhang, *Chem. Rev.*, 1995, **95**, 1191; G. A. Olah, G. Rasul, X. Y. Li and G. K. S. Prakash, *Bull. Soc. Chim. Fr.*, 1995, **132**, 569; Z. Xie, R. Bau, A. Benesi and C. A. Reed, *Organometallics*, 1995, **14**, 3933; L. Olsson, C. H. Ottosson and D. Cremer, *J. Am. Chem. Soc.*, 1995, **117**, 7460; M. Arshadi, D. Johnels, U. Edlund, C. H. Ottosson and D. Cremer, *J. Am. Chem. Soc.*, 1996, **118**, 5120; Z. Xie, J. Manning, R. W. Reed, R. Mathur, P. D. W. Boyd, A. Benesi and C. A. Reed, *J. Am. Chem. Soc.*, 1996, **118**, 2922; J. B. Lambert and Y. Zhao, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 400; H. U. Steinberger, T. Müller, N. Auner, C. Maerker and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 626; P. v. R. Schleyer, *Science*, 1997, **275**, 39; J. Belzner, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1277; C. A. Reed, *Acc. Chem. Res.*, 1998, **31**, 325.
31 J. Chojnowski, W. Fortuniak and W. Stanczyk, *J. Am. Chem. Soc.*, 1987, **109**, 7776; J. Chojnowski and W. Stanczyk, *Adv. Organomet. Chem.*, 1990, **30**, 243.
32 Y. Apeloig, O. Merin-Aharoni, D. Danovich, A. Ioffe and S. Shaik, *Isr. J. Chem.*, 1993, **33**, 387.
33 H. Tashiro, K. Kikukawa, K. Ikenaga, N. Shimizu and M. Mishima, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2435.

34 E. Pretsch, W. Simon, J. Seibl and T. Clerc, *Tables of Spectral Data for Structure Determination of Organic Compounds*, Springer-Verlag, Berlin-Heidelberg, 2nd Edn., 1989.
35 gNMR from Cherwell Scientific Publishing Limited, The Magdalen Centre, Oxford Science Park, Oxford, UK OX4 4GA.
36 M. P. Doyle, C. C. McOsker and C. T. West, *J. Org. Chem.*, 1976, **41**, 1393.
37 D. J. Watkin, J. R. Carruthers and P. W. Bettridge, *CRYSTALS. User Guide*, Chemical Crystallography Laboratory, University of Oxford, 1988.
38 J. Pearce, D. J. Watkin and D. P. Prout, *CAMERON. A Program for Plotting Molecular Structures*, Chemical Crystallography Laboratory, University of Oxford, 1992.

Paper 9/03303C